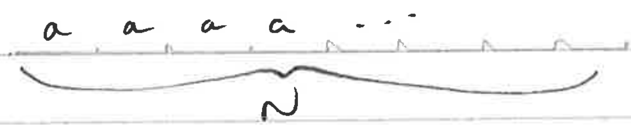
Collapse Transition of a Phantom Polymer

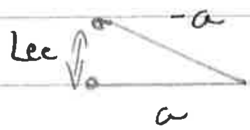
24/10/24 Consider a polymer made of N bonds each of length a in 1D.
Let each bond have two states: $+a$ or $-a$:

max length: $L_0 = Na$



Bonds can flip:

Each flipped bond reduces the end-to-end length by $2a$:



original $L_{ee} = 2a$
Flipped $L_{ee} = 0$

Let there be M flipped bonds out of N:

$$\Rightarrow \quad L_{ee} = (N - 2M).a$$

The number of states of the polymer with M flips in N bonds is:

$$\Omega(N, M) = \frac{N!}{M!(N-M)!}$$

Why? Because any bond can be flipped independently of all the others.

We assume the energy cost of flipping a bond is zero, and that thermal fluctuations make the polymer explore all of its possible conformations.

$\Rightarrow$ Polymer spends most time in the state with the largest number of microstates.

$$F = \cancel{E}^{\,0} - TS = -TS = -k_B T \ln \Omega(N, m)$$

$$\therefore F = -k_B T \ln \left[\frac{N!}{m!(N-m)!} \right]$$

Let $N, m \gg 1$, we want to know the free energy and the most probable state of the polymer.

Stirling's approx. $\ln N! \sim N \ln N - N + \cancel{\tfrac{1}{2} \ln(2\pi N)}^{\,0}$

$$\Rightarrow -\beta F = \ln N! - \ln m! - \ln(N-m)!$$

$$= N \ln N - N - (m \ln m - m) - [(N-m)\ln(N-m) - (N-m)]$$

$$= N \ln N - \cancel{N} - m \ln m + \cancel{m} - (N-m)\ln(N-m) + \cancel{N} - \cancel{m}$$

$$= N \ln N - m \ln m - (N-m)\ln(N-m)$$

Let $L_0 = Na$ $\Rightarrow$ $\boxed{N = \frac{L_0}{a}}$

$L = (N-2M)a$

and $\boxed{M = \frac{L_0 - L}{2a}}$

which also gives: $\boxed{N - M} = \frac{L_0}{a} - \frac{(L_0-L)}{2a} = \frac{2L_0 - L_0 + L}{2a} = \boxed{\frac{L_0+L}{2a}}$

so, $-\beta F = N\ln N - M\ln M - (N-M)\ln(N-M)$

$$= \left(\frac{L_0}{a}\right)\ln\left(\frac{L_0}{a}\right) - \left(\frac{L_0-L}{2a}\right)\ln\left(\frac{L_0-L}{2a}\right) - \left(\frac{L_0+L}{2a}\right)\ln\left(\frac{L_0+L}{2a}\right)$$

$$= \frac{L_0}{a}\left[\ln\left(\frac{L_0}{a}\right) - \left(\frac{1-L/L_0}{2}\right)\ln\left(\frac{L_0-L}{2a}\right) - \left(\frac{1+L/L_0}{2}\right)\ln\left(\frac{L_0+L}{2a}\right)\right]$$

Let $x = L/L_0$

$$= \frac{L_0}{2a}\left[2\ln\left(\frac{L_0}{a}\right) - (1-x)\ln\left(\frac{L_0}{2a}(1-x)\right) - (1+x)\ln\frac{L_0}{2a}\left((1+x)\right)\right]$$

$$= \frac{L_0}{2a}\left[2\ln\left(\frac{L_0}{a}\right) - (1-x)\ln(1-x) - (1-x)\ln\left(\frac{L_0}{2a}\right) - (1+x)\ln(1+x) - (1+x)\ln\left(\frac{L_0}{2a}\right)\right]$$

cancel leaving $+2\ln 2$

cancel

$$-\beta F = \frac{L_0}{2a}\Big[\cancel{2\ln\left(\frac{L_0}{a}\right)} - (1-x)\ln(1-x) - (1+x)\ln(1+x)$$

$$- \cancel{(1-x)}\ln\left(\frac{L_0}{a}\right) + \cancel{(1-x)}\ln 2$$

$$- \cancel{(1+x)}\ln\left(\frac{L_0}{a}\right) + \cancel{(1+x)}\ln 2 \Big]$$

$$-\beta F = \frac{L_0}{2a}\left[-(1-x)\ln(1-x) - (1+x)\ln(1+x) + 2\ln 2 \right]$$

$$\therefore \beta F = \frac{L_0}{2a}\left[(1-x)\ln(1-x) + (1+x)\ln(1+x) - 2\ln 2 \right]$$

$$\therefore \boxed{F = k_B T \frac{L_0}{2a} f(x)} \quad \text{where } f(x) = (1-x)\ln(1-x) + (1+x)\ln(1+x) - 2\ln 2$$

NOTES

1) $F \propto k_B T \Rightarrow$ Entropic Force $\equiv$ entropic spring

2) $F \propto \frac{L_0}{a} = N = \#$ of bonds

3) What does $f(x)$ look like?

4) minimum in Free energy is for $x = 0$, i.e. Spring has zero length

If $x << 1$ i.e. $L << L_0$

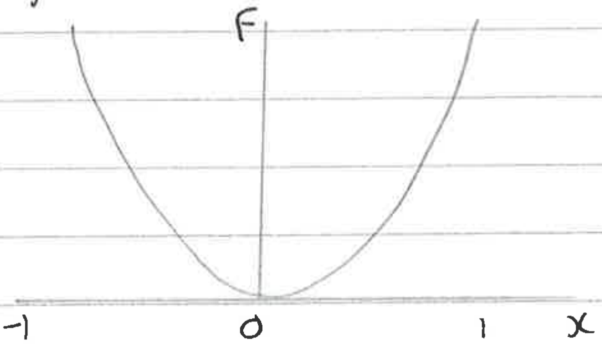
$$\Rightarrow \ln(1-x) \sim -x$$
$$\ln(1+x) \sim x$$

$$\Rightarrow f(x) \sim (1-x).-x + (1+x).x - 2\ln 2$$

$$= 2x^2 - 2\ln 2$$

$$\therefore F(x) = \frac{k_B T L_0}{2a}.(2x^2 - 2\ln 2) \sim \frac{k_B T . L_0}{a} x^2 + \text{const. indep. of } x$$

$\therefore$ Free energy is quadratic in the relative end-to-end length



Suppose we apply a force F_{ext} to the spring, how does it respond?

$$\text{Force} \propto \frac{-\partial F}{\partial L} = \frac{-\partial F}{\partial x} . \frac{dx}{dL} = \frac{-1}{L_0} \frac{\partial F}{\partial x}$$

$$= \frac{-1}{\cancel{L_0}} \frac{k_B T \cancel{L_0}}{2a} \frac{\partial f(x)}{\partial x}$$

$$\frac{\partial F}{\partial x} = -1.\ln(1-x) + (1\cancel{-}x).\frac{1}{1\cancel{-}x}.-1 + 1.\ln(1+x) + (1+x).\frac{1}{1+x}.1$$

$$= -\ln(1-x) - 1 + \ln(1+x) + 1$$

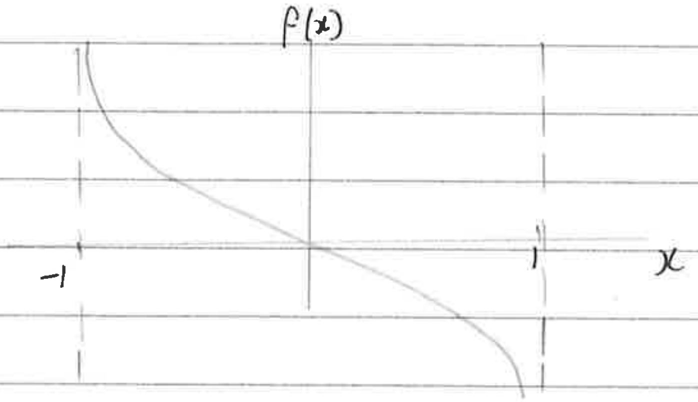
$$= \ln\left(\frac{1+x}{1-x}\right)$$

$$\therefore \text{Force} = -\frac{k_BT}{2a}\ln\left(\frac{1+x}{1-x}\right) \quad \text{or} \quad \boxed{\text{Force} = \frac{k_BT}{2a}\ln\left(\frac{1-x}{1+x}\right)}$$

Force exerted by the spring if we stretch it by a distance x.

Notes

1) Force at $x=0$ is 0
2) Force $\to \pm\infty$ as $x \to \pm 1$
3) Force $\propto k_BT$, hence entropic spring
4) Force is linear near $x=0$



For $x \sim 0 \Rightarrow$ Force $\sim \frac{k_BT}{2a}\left(-2x + \ldots\right) = -\frac{k_BT}{a}x$ i.e. Linear in x.

Pulling an entropic spring

What if we pull on the spring?

We make bond flips less likely, so it raises free energy.

$$F = U - TS = \alpha m - k_B T \ln\left[\frac{N!}{m!(N-m)!}\right]$$

The only difference to the solution is:

$$F = \alpha\left(\frac{L_0 - L}{2a}\right) + \frac{k_B T L_0}{2a}\left[(1-x)\ln(1-x) + (1+x)\ln(1+x) + \text{const}\right]$$

$x = \frac{L}{L_0}$

$$= \frac{\alpha L_0 (1-x)}{2a} + \frac{k_B T L_0}{2a}\left[\quad " \quad\right]$$

and again, we get the force by differentiating.

$$\text{Force} = -\frac{\partial F}{\partial L} = -\frac{\partial x}{\partial L}\cdot\frac{\partial F}{\partial x} = -\frac{1}{L_0}\left[\frac{-\alpha L_0}{2a} + \frac{k_B T L_0}{2a}\ln\left(\frac{1+x}{1-x}\right)\right]$$

$$= \frac{\alpha}{2a} + \frac{k_B T}{2a}\ln\left(\frac{1-x}{1+x}\right) = 0 \text{ in equilibrium.}$$

$$\Rightarrow \ln\left(\frac{1-x}{1+x}\right) = -\beta\alpha$$

$$\Rightarrow \frac{1-x}{1+x} = e^{-\beta\alpha}$$

$$\Rightarrow (1-x) = (1+x)e^{-\beta\alpha}$$

$$\Rightarrow (1-e^{-\beta\alpha}) = x(1+e^{-\beta\alpha})$$

$$\therefore x = \frac{1-e^{-\beta\alpha}}{1+e^{-\beta\alpha}} \qquad \times \text{ by } e^{\frac{1}{2}\beta\alpha}$$

$$= \frac{e^{\frac{1}{2}\beta\alpha} - e^{-\frac{1}{2}\beta\alpha}}{e^{\frac{1}{2}\beta\alpha} + e^{-\frac{1}{2}\beta\alpha}} = \operatorname{Tanh} \tfrac{1}{2}\beta\alpha$$

$$\therefore \frac{L}{L_0} = \operatorname{Tanh}\left(\frac{\alpha}{2k_BT}\right)$$